Chapter 3

Characterization of Semiconducting Block Copolymers in Solution

Abstract

The influence of the solvent temperature and the solvent quality on the chain conformation and the aggregation of semiconducting block copolymers is described in this Chapter. Decreasing the temperature of a chloroform solution of PPV-b-PS hardly affected the conformation of the block copolymer. However, when CS₂ was used as a solvent, its cooling resulted in aggregation of PPV-b-PS, manifested by an additional photoluminescence band (630 nm) at the red edge of the PL spectrum.

Upon addition of a selective solvent (acetone) for the polystyrene block to a solution of PPV-b-PS in chloroform (good solvent for both blocks), a new PL maximum (575 nm) and a shoulder (625 nm) were observed. The PL spectrum of the semiconducting block copolymer in a mixture of chloroform and acetone resembled the PL spectrum of a thin film cast from chloroform. The solution PL spectra are composites of single-molecule contributions (peaking around 540 nm) and aggregate contributions. This confirms the idea of micelle formation, where such particles are in dynamic equilibrium with single molecules; the concentration of the latter remains fixed at the, so-called, critical micelle concentration. Small angle neutron scattering experiments supported the concept of aggregation (micelle formation) of the PPV-b-PS diblock copolymers in solvent mixtures of chloroform and acetone.

The work presented in this Chapter is covered by the following paper:
3.1 Introduction

PPVs are widely studied for their semiconducting and luminescent properties in the solid-state. For the processing of PPVs into thin films, they are modified with solubilizing side-chains that allow spin coating and drop casting from common organic solvents, leading to uniform, large-area, optical-quality films. The ease of processing polymers compared to conventional inorganic semiconductors offers the potential for cost-saving in applications that require visible band-gap semiconductors. Despite the advantages and versatility of polymer processing for opto-electronic applications, the fundamental physics underlying the construction or optimization of practical devices remains poorly understood. One controversy concerns the difference of the excited state in solution and in the solid-state. When the chains of a conjugated polymer are isolated in dilute solution, it is well accepted that photoexcitation creates only one electronic species; the singlet intrachain exciton.\(^1\)\(^-\)\(^4\) In the solid film, however, the polymer chains are in contact and the estimate of the number of primary photoexcitations that result in interchain species ranges from almost zero\(^5\) to 90\%.\(^6\) The species in solution and solid-state represent the two extreme situations of highly diluted chains and close-packed chains, respectively. During processing of conjugated polymers, the concentration profile will change from dilute solution to the solid-state and at some intermediate state the individual chains will affect each other and interact (aggregation). At high concentration or in the solid-state this results in the coexistence of intra- and intermolecular excited states.

Aggregation in solutions of PPV-derivatives has been observed and the spectroscopic characteristics of the more common polymers (MEH-PPV,\(^3\)\(^,\)\(^7\)\(^-\)\(^10\) DOO-PPV\(^11\)) in various solvents as well as of the films produced from them have been quite extensively studied. Both temperature and solvent quality dramatically affect the wavelength (photon energy) of photoluminescence (PL) and the PL efficiency in solution\(^10\)\(^-\)\(^\)\(^13\) and affect the opto-electronic properties of the polymer film as well. For example, the luminescence from a solution of DOO-PPV in toluene was found to be gradually quenched upon cooling below room temperature, which was attributed to a strong reduction in solubility and the concomitant formation of aggregates.\(^11\) The relative importance of intrachain and interchain (intersegment) interactions with respect to electronic excitations in polymer systems is still a topic of great interest as well as controversy.\(^10\)\(^-\)\(^17\)

In the case of diblock copolymers, the different solubilities of the two blocks in a given solvent will undoubtedly lead to a rich phase behavior. In an environment that preferentially dissolves one of the blocks, aggregation of the other block is expected to give rise to the formation of micelles or even more complex mesophases.\(^18\) In the DOO-PPV-based diblock copolymers described in this study, the PPV blocks could form the core of the micelles, and in view of their stiffness and restricted length they might well form lyotropic nematic domains in specific solvents. The substitution pattern on the PPV block plays an important role in this respect.
The suitability of the block copolymers, described in Chapter 2, for application in photovoltaic devices relies, among other things, on the abilities of the respective blocks to function as electron donor and acceptor, and as charge transport media. As outlined in Chapter 1, the structure and morphology of the solid are crucial factors to both these functions. Both local order and morphology of a thin film obtained from a polymer solution by means of casting procedures will reflect the chain's microstructure, i.e., its conformation, entanglement topology, and the local order of aggregated segments, just prior to solidification or vitrification. The solidification process will proceed far from equilibrium conditions because of several factors, such as the temperature gradients caused by a rapid evaporation of solvent at the film surface, the accompanying concentration gradients and diffusive transport, and, in the case of spin-casting, bulk flow patterns. Admittedly, all these processes will certainly affect the microstructure during the transition from solution to solid film. The essential parameters governing the process may be assessed in first approximation, though only with caution, from a study of aggregation and solidification behavior as a function of solvent quality and temperature under equilibrium conditions.

3.2 Temperature dependence of UV–vis and photoluminescence of semiconducting block copolymers

Figure 3.1 shows the temperature dependence of the UV–vis absorption and photoluminescence of PPV$_{3.6k}$-b-PS$_{24.8k}$ (2 × 10$^{-1}$ mg/ml) in chloroform and in carbon disulfide (CS$_2$). Clearly, in chloroform, both the absorption and fluorescence spectra do not change significantly upon cooling the solution from room temperature to –20 °C, indicating that chloroform remains a fairly good solvent for the whole block copolymer chain over this temperature range. The slight red shift may be due to a reduction of thermal motions such as ring librations and hence a slight increase in conjugation (length). Relative to the spectra in chloroform at the same temperature, the spectra obtained from solutions of the block copolymer in CS$_2$ are red-shifted (solvatochromic shift$^{19}$). The temperature dependence of the peak wavelengths is slightly stronger in the latter solvent, but qualitatively similar. Since absorption and luminescence curves show equal shifts, these spectra are predominantly of single-molecule origin. Chain conformation adjustments as well as stabilization of the excited state by dipole rearrangements and induced-dipole effects are the likely cause of these thermochromic shifts. The only remarkable feature is the emergence of an additional band around 630 nm upon cooling of the solution in CS$_2$. Similarly, Hsu et al. found that the solubility of DOO-PPV in toluene solution strongly depends on the temperature when cooled below room temperature.$^{11}$ They attributed the appearance of the additional band in the PL spectrum to the formation of interchain aggregated states. On the basis of their investigation and our own additional results, described in Sections 3.3 and 3.4, we attribute the peak at 630 nm to emission from an
aggregated state. Since CS$_2$ dissolves polystyrene rather selectively, especially at lower temperatures, it seems reasonable to expect some form of aggregation of the PPV blocks.

Figure 3.1  $UV$–vis absorption and photoluminescence spectra of PPV$_{3.6k}$-b-PS$_{24.8k}$ as a function of temperature in chloroform and carbon disulfide.
3.3 Solvent quality dependence and aggregation of semiconducting block copolymers

Instead of employing different solvents, the quality of the medium can be varied by adding a poor solvent to a good solvent. Figure 3.2 shows the results of increasing the fraction of acetone, a non-solvent for PPV, in a chloroform/acetone mixture containing $2 \times 10^{-2}$ mg/ml PPV-$b$-PS. Since both these liquids are good solvents for polystyrene, one expects a much reduced solubility only for the PPV blocks in such a mixture. For a more detailed description, one would have to take preferential solvation into account, but this will be neglected in our discussion.

![Normalized UV–vis absorption and photoluminescence spectra of PPV$_{3.6k}$-$b$-PS$_{24.8k}$ in chloroform, in chloroform/acetone mixtures and as cast film.](image)

The absorption spectra, little detailed as they are, broaden with increasing acetone content. While the maximum shifts slightly to the blue, the tail of the red edge moves out considerably. A blue shift is also observed for the fluorescence maximum initially at 540 nm; it moves about 0.07 eV. At higher acetone content, the fluorescence spectra have
become more structured, and this is of great help in setting up the simplest model that is consistent with our results. The PL maximum and shoulder around 575 nm (2.15 eV) and 625 nm (1.98 eV) can be easily taken as belonging to the vibronic progression (of 0.17 eV). However, we think that such a change in the Frank–Condon envelope is not plausible. It is proposed that these emerging features are actually a manifestation of a different species, an aggregate formed upon decreasing the solvent quality for the PPV block. This idea is supported by the spectrum obtained for the cast film: its PL has maxima at the aforementioned energies. Given the level of detail in the PL spectrum from this species, it is probably quite well-defined from point of view of structure. The solution PL spectra are composites of single-molecule contributions (peaking around 540 nm) and aggregate contributions. This corroborates the idea of micelle formation, where such particles are in dynamic equilibrium with single molecules (unimers); the concentration of the latter remains fixed at the, so-called, critical micelle concentration. While a change in polymer concentration will merely change the number ratio between the two species, a change of the thermodynamic conditions may affect the structure and size of the micelle (see next Section). The PL spectrum of the cast film has contributions from aggregate structures only. This does not imply that interchain arrangements are particularly uniform throughout this solid film, but ultrafast energy migration will ensure that the lowest-energy sites exclusively contribute to the PL. Not so for the absorption spectrum of the film, however, which is also broadened with respect to the spectrum from chloroform solution, and quite similar to the spectra from the mixed-solvent solutions. An extension on both the blue and the red sides of the single-molecule spectrum is attributed to H-type aggregation and understood as modeled by Kasha et al.\textsuperscript{20} Dipole–dipole interactions in the excited state lead to a level splitting in which the higher level (blue-shifted) is one-photon allowed and the lower level (red-shifted) is one-photon forbidden. Any deviation from the strict H-type arrangement, or disorder, introduces a finite transition probability from the ground state to the lower-level excited state. This explains the tailing of the red edge of the absorption spectra. For the PL, the lower-lying aggregate state is the only relevant state, because of ultra-fast internal conversion from the higher state. Note that inhomogeneous broadening due to disorder is limited in the solid, as a result of energy diffusion. Since emission from the lower state has a low probability in H-type aggregates, it remains very relevant within the context of opto-electronic properties to measure the lifetime and quantum efficiency of this state,\textsuperscript{21} to assess the relative importance of the various possible deactivation pathways.

We have assessed the photoluminescence decay at 535, 585 and 630 nm upon excitation at a wavelength of 465 nm, using a Hamamatsu streak camera. All three experimental curves were fitted well with a biexponential law. For each of the three wavelengths we found similar time constants ($\tau_1 = 240 \pm 40$ ps; $\tau_2 = 710 \pm 20$ ps), and approximately equal weights as well. The spectral overlap between the two components prevented a more accurate determination of the individual contributions. Further
experiments are necessary to resolve these components and to assess whether or not additional, weaker components are present.

Similarly to the UV–vis absorption and photoluminescence spectroscopy studies presented above, the macroinitiator PPV-TIPNO was investigated in solvent mixtures of chloroform and acetone ($2 \times 10^{-2}$ mg/ml). The UV–vis spectra demonstrated the same broadening at the red edge upon increasing the acetone content and the PL spectra showed the appearance of additional PL bands at 590 and 630 nm. For PPV-TIPNO, however, these features already appeared after adding 30 volume-% acetone, whereas it required 80 volume-% acetone to produce appreciable changes in the spectra of the block copolymer system. Moreover, the block copolymer (PPV-b-PS) was still soluble for a considerable time in a mixture of 10 volume-% chloroform and 90 volume-% acetone, in contrast to the PPV-based macroinitiator, which precipitated when more than 40 volume-% acetone was added. This difference indicates that selective solubility of the PS block by acetone enhances the overall solubility of the block copolymer.

In the case of PPV-b-P4VP (synthesis described in Section 2.3.3), similar spectra were obtained by using a dilute solution ($2 \times 10^{-2}$ mg/ml) in solvent mixtures of chloroform and methanol, where methanol is a selective solvent for the block of poly(4-vinylpyridine). The same arguments and reasoning as above hold for these block copolymers.

### 3.4 Small angle neutron scattering of semiconducting block copolymers in solvent mixtures

For a further characterization of the aggregation behavior of PPV$_{3.6k}$-b-PS$_{24.8k}$, small-angle neutron scattering (SANS) was used to determine the size of the aggregates. The experiments were carried out at the pulsed neutron source at ISIS, UK. In these experiments, mixtures of deuterated chloroform and deuterated acetone were employed to vary the solvent quality and we explored the range of 0–50 volume-% acetone. To obtain practicable exposure times, a polymer concentration of 2 mg/ml (ca. 0.2 weight-%) was used, which is a hundred times as high as that for the spectroscopic measurements. With exposure times of 1.5 to 4 hours per sample, the counting statistics are still moderate, especially at high CDCl$_3$ content, due to neutron absorption by the chlorine atoms. Figure 3.3 shows the data evaluated by fitting to model curves calculated by means of the program FISH, assuming a spherical core–shell particle with an additional transition layer between core (PPV part of block copolymer molecules) and shell (PS blocks, swollen). The shell has a ramp profile as well (Figure 3.3 inset), which is a simple representation of the decreasing concentration in a polymer brush.
Figure 3.3  Small-angle neutron scattering data (log–log) of PPV\(_{3.6k}\)-b-PS\(_{24.8k}\) block copolymer in CDCl\(_3\)/acetone-d\(_6\) mixtures (symbols) and model fits (lines). Inset: density profile for 3-radius spherical-particle model used in fitting.

The results indicate an increase of both \(r_{\text{inter}}\) and \(r_{\text{shell}}\) with increasing acetone content, suggesting an increase in the number of aggregated chains per micelle. The size of the dense core \((r_{\text{core}})\) is probably around 2.5 nm; it is less well defined by the data, which have a usable scattering vector range \(q = 0.1–1.9\) nm\(^{-1}\). An additional measurement of a 0.1 weight-% polymer solution in the 1:1 solvent mixture yielded dimensions similar to those found for the 0.2 weight-% solution, which supports the idea of micelle formation. The calculated density contrasts are not entirely consistent yet with the simple picture of solid core and swollen shell. The discrepancy between measured data and fit at the smallest angles may indicate that a more elongated particle shape\(^{24}\) or polydispersity are the source of the deviations. Although the current data do not warrant more detailed modeling, it supports the concept of aggregation of the PPV-b-PS diblock copolymers in solvent mixtures of chloroform and acetone.

All results described in the three previous Sections, are consistent with the formation of aggregated species in solution. By changing the solvent temperature or the solvent quality for diblock copolymers in solution, they reorganize from single, non-interacting chains to
aggregated clusters of polymer chains. Both variables (solvent temperature and solvent quality) are dramatically changing during casting procedures, due to the rapid evaporation of solvent, which, in turn, results in cooling of the solvent and a continuous increase of the concentration. Hence, the casting conditions can have a dramatic effect on the morphology of the thin film and, consequently, on the device performance.

### 3.5 Experimental

**Measurements**

UV–vis spectra were recorded on a Perkin–Elmer Lambda 900 spectrometer and normalized for clarity. Reduced-temperature UV–vis and photoluminescence spectra were recorded under argon by using an Oxford cryostat equipped with four optical windows. Temperature dependent photoluminescence spectra were recorded with a Chromex optical multi-channel analyzer. A typical integration time of 5000 ms was used. As a source for the PL excitation, the Perkin–Elmer Lambda 900 was employed. The spectrometer was set at zero wavelength (white light) and a band-pass filter was used to obtain a light beam spanning 375–550 nm. The PL spectra were recorded under a 90° angle with respect to the incoming light. The obtained data were corrected for the spectral response of the Chromex optical multi-channel analyzer. Photoluminescence spectra of diblock copolymers in solvent mixtures were recorded on a Perkin–Elmer LS50-B spectrofluorimeter with the excitation wavelength at the absorption maximum. The photoluminescence decay at 535, 585 and 630 nm upon excitation at a wavelength of 465 nm were recorded using a Hamamatsu streak camera. All spectra were recorded using a 10 × 10 mm quartz cells. SANS data were recorded on the LOQ instrument installed at the pulsed neutron source at ISIS (Rutherford Appleton Laboratory), UK. It uses time-of-flight detection of neutrons covering a wavelength of 0.22–1.0 nm.

**Materials and methods**

Chloroform and acetone for spectroscopy purposes were of UV–vis grade. All solvents and deuterated solvents were used as received. For spectroscopy in solvent mixtures, a stock solution of polymer of 1 × 10^{-1} mg/ml in chloroform was prepared. The stock solution was diluted first with chloroform and then the appropriate amount of acetone was added. The vials were shaken for 30 minutes before spectra were recorded. Thin films were prepared by drop-casting the stock solution on quartz.
3.6 References
